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TECHNICAL REPORT RDMR-WD-14-41

MODELING NANOCOMPOSITES FOR MOLECULAR DYNAMICS (MD) SIMULATIONS

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Aviation and Missile Research, Development,
and Engineering Center

January 2015

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REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 2015	Final

4. TITLE AND SUBTITLE

Modeling Nanocomposites for Molecular Dynamics (MD) Simulations

5. FUNDING NUMBERS

6. AUTHOR(S)

Ebonee A. Walker

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Commander, U.S. Army Research, Development, and
   Engineering Command
ATTN: RDMR-WDG
Redstone Arsenal, AL 35898-5000

8. PERFORMING ORGANIZATION REPORT NUMBER

TR-RDMR-WD-14-41

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

A

13. ABSTRACT *(Maximum 200 Words)*

The minimum energy configuration for Molecular Dynamics (MD) simulations is found for a carbon nanotube (CNT)/polymer composite that is modeled using the Tersoff-Brenner and Reactive Empirical Bond Order (REBO)/Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) interatomic potentials. The Tersoff-Brenner potential is used to model C-C bonding and the REBO/AIREBO for non-bonding interactions. Using polyethylene (PE) monomers, the appropriate bonding coefficients are identified for a stable, low energy nanocomposite.

14. SUBJECT TERMS

Nanocomposites, Carbon Nanotubes (CNTs), Molecular Dynamics Simulations

15. NUMBER OF PAGES

18

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

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I. INTRODUCTION

Improving heat dissipation is of interest to many applications, especially electronics. As the size of electrical components continues to decrease, the amount of heat generated in the components increase. Composite materials, in which many electronics are embedded, have shown poor performance dissipating heat generated by electrical components. For instance, carbon fiber composites have gained wide use in automotive-to-munition-to-athletic applications because of their strength and light weight; however, their heat dissipation is poorer than the metals they replace. To overcome this bottleneck, techniques like Transient Liquid Phase Sintering (TLPS) and nanoparticles have been used to improve heat dissipation from carbon fibers. To improve heat dissipation in carbon fiber composites, interactions at the interface of these materials require further understanding.

Composites combine two or more materials with different properties to yield a material with unique properties [1]. Nanocomposites are a class of composites which contain at least one material with at least one nanoscale dimension. Nanoscale fillers have properties that can be different from their bulk material due to size effects. In studies, nanocomposites have shown improved electrical, mechanical, and thermal properties. Carbon fiber composites have shown success in improving mechanical properties. Carbon nanotube (CNT)-based nanocomposites have been studied for integration with carbon fiber composites to improve heat transport.

Carbon fibers, like other carbon allotropes, have poor thermal transport in transverse directions (out of and across fiber planes) but excellent transport in longitudinal (along the fiber) directions. In most applications, carbon fibers are combined with an epoxy. Epoxy is a thermosetting polymer that, like the carbon fiber, has poor thermal conductivity; however, carbon fiber reinforced epoxy composites are strong and lightweight. Since neither carbon fiber nor epoxies possess high thermal transport, several studies have focused on how to improve heat dissipation in the carbon fiber composite. Techniques have varied based on the method of production for the carbon fiber composites. In the case of filament wound carbon fibers composites, efforts have focused on modifying the epoxy which acts as the bonding agent holding the fibers together.

Molecular Dynamics (MD) simulations can be used to track the trajectory of individual atoms and/or molecules. By applying the appropriate interatomic potential to govern the interactions of the atoms, MD simulations can be used to understand the thermal transport at the interface of materials. Since MD simulations calculate atom positions, properties such as kinetic energy, dispersion, and thermal conductivity can be deduced.

II. THEORY

Thermal conductivity can be calculated using MD simulations by application of Fourier's law of heat conduction:

$$\kappa = \frac{1}{A} \cdot \frac{\Delta Q}{\Delta t} \cdot \frac{dT}{dx}$$

where, κ is the thermal conductivity of the system, A is the cross-sectional area, $\Delta Q/\Delta t$ is the rate of energy transfer, and dT/dx is the temperature gradient. The area and simulation time of the

system are known values. In Non-Equilibirum Molecular Dynamics (NEMD) simulations, two methods can be used to generate a temperature gradient. The first method establishes a constant temperature difference in the system and calculates the energy transferred in the system. Alternatively, the energy applied to the system can be constant and the temperature gradient calculated.

The constant energy method is used in this report. To cause a temperature difference, a constant amount energy, Q, is added and subtracted from heat baths. The addition of energy raises the temperature of the slab. Conversely, subtracting lowers the slab's temperature. Figure 1 shows the simulation's arrangement where the heat baths are located at 0.25 and 0.75 of the system's total length [2], which allows a temperature gradient to be established without the heat baths being located next to one another. The energy must be divided by half for calculating thermal conductivity because, in this technique, the energy can flow in two directions from the baths. The system is divided into slabs of equal thickness in the longitudinal direction. The temperature gradient is calculated based on statistical mechanics. If the kinetic energy, KE, of an atom is known, then the temperature of that atom is $T=2(KE)/3k_B$, where k_B is Boltzmann's constant. The temperature of each slab is calculated by averaging together the temperatures of the atoms within that slab. For Fourier's law to be applicable, the temperature gradient produced must be linear.
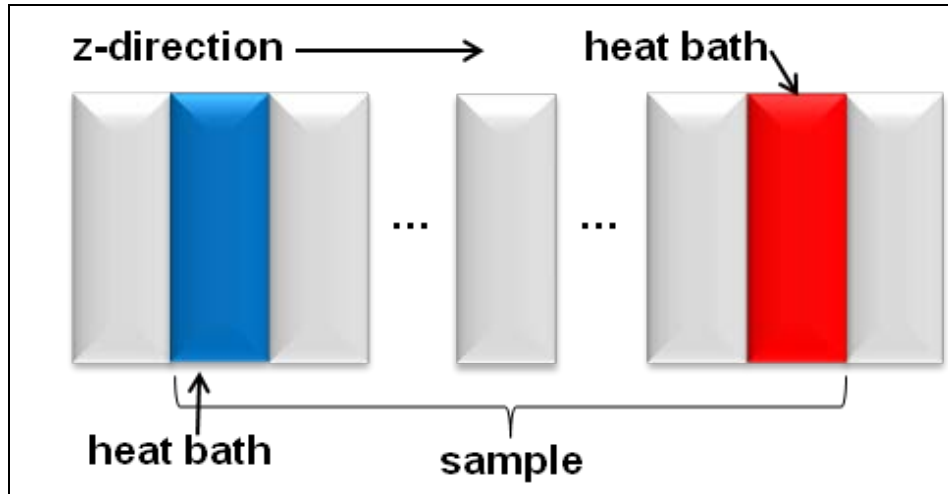
Figure 1. NEMD Setup for Constant Energy Temperature Gradient

III. NANOCOMPOSITE MODEL

The flowchart of a MD simulation is shown in Figure 2. The initial step in the simulation is to assign the coordinates for each atom. Two software packages were used to generate the initial coordinates for the nanocomposite: TubeGen and Packmol [3, 4]. TubeGen was used to generate the initial configuration for CNTs. An example TubeGen script is shown in the appendix which would produce the coordinates for a (10, 10) Single-Wall Nanotube (SWNT), which is frequently used in MD simulations [5]. Figure 3 shows a cartoon representation of the coordinates using Visual Molecular Dynamics (VMD) [6].

Give atoms initial positions $r^{(t=0)}$, choose short Δt
Get forces $\boldsymbol{F} = - \nabla V(\boldsymbol{r}^{(i)})$ and $\boldsymbol{a} = \boldsymbol{F}/m$
Move atoms: $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)} \Delta t + \frac{1}{2} \boldsymbol{a} \Delta t^2 + \ldots$
Move time forward: $t = t + \Delta t$
Repeat as long as you need

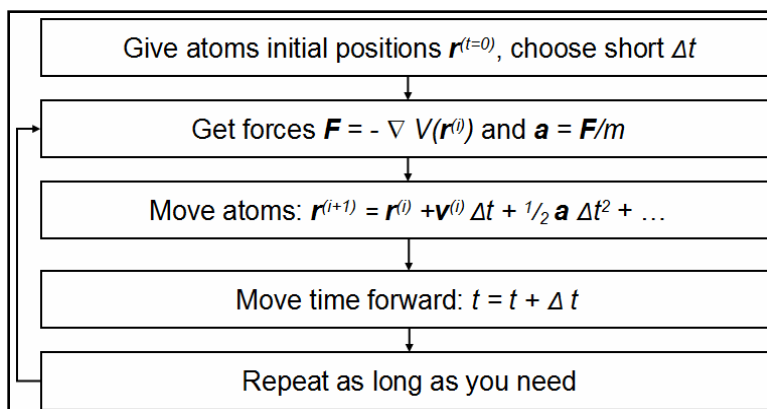*Figure 2. Description of MD Simulation Algorithm [7]*
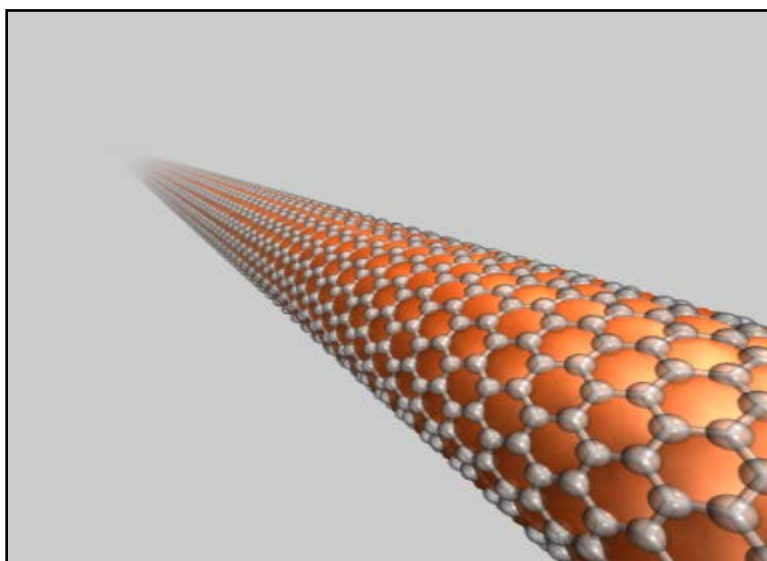
Figure 3. VMD Rendering of (10,10) SWNT From Coordinates Generated by TubeGen

Similarly, Packmol can be used to generate the polymer molecules' initial coordinates by taking the coordinates of a typical molecule, like ethylene (Figure 4), and finding the most efficient packing. Using the Protein Data Bank (PDB) [8], the coordinates of myriad atoms can be found. An example script for Packmol to pack ethylene molecules into a 80-by-80-by-100 nanometer box with a cylindrical void in the center to house the CNT is shown in the appendix. Since a Large-Scale Atomic and Molecular Massively Parallel Simulator (LAMMPS) is used as the MD simulator [9], the coordinates must be formatted for use in LAMMPSs. VMD has a set of tools (TopoTools) that can be used to generate a LAMMPS-readable format [6].

*Figure 4. Ethylene Monomer Produced From Coordinates in PDB
and Rendered Using VMD (Green, C Atoms; Gray, H Atoms)*
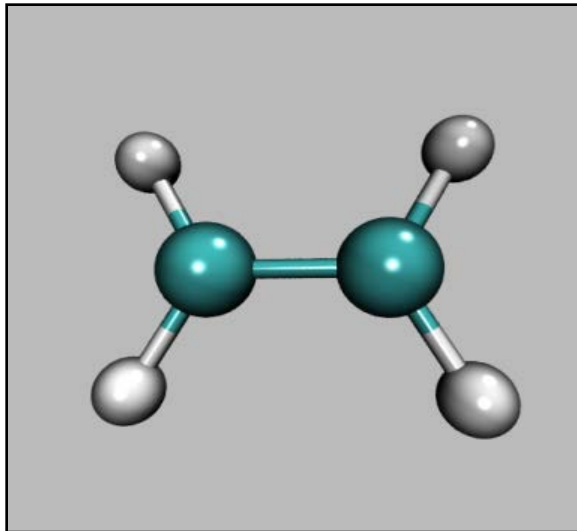
To achieve meaningful results from a MD simulation, the appropriate interactions must occur between the atoms. The forces between atoms are governed by the interatomic potential. Several interatomic potentials, also known as force fields, exist. The differences in potentials arise from how the parameters of the potential were fitted. Some potentials are based on experimental data, whereas others come from quantum mechanics calculations. The Tersoff and Reactive Empirical Bond Order (REBO)/Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potentials are used regularly for MD simulations involving thermal conductivity and CNTs since they describe covalent bonds [10]. For the present simulations, AIREBO will be used since it addresses the interactions of not only carbon (C) atoms, but also hydrogen (H) atoms. Additionally, the van der Waals interaction of the CNT with the polymer and of polymer chains is described by the Lennard-Jones potential.

Finally, simulations are performed by advancing the atoms and recalculating the forces. A time step is chosen that provides stable simulations, yet does not require a large amount of computational time. Time steps on the order of a femtosecond are usually sufficient for tracking phonons; however, the H atoms can sometimes cause high frequencies that require smaller time steps. Simulations usually require an equilibration period to allow the total energy of the system to stabilize. After stabilization, the desired properties can be calculated.

IV.   SIMULATION SETUP

The (10,10) SWNT and polyethylene (PE) are used to model nanocomposite for thermal conductivity measurements. The (10,10) SWNT is chosen because the diameter of 1.4 nanometers is reported as a typical size for SWNTs [5]. PE is a simple hydrocarbon, yet it is applicable since polymers generally have low thermal conductivities. Its purpose is to show the trend of interacting with the CNT. The CNT and PE are generated for a length of 100 nanometers.

The Lennard-Jones potential describes the interactions of non-bonded atoms. The Lennard-Jones potential, U, is given by the following:

$$U = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

where, ε is the depth of the potential well, σ is the distance at which the potential energy is zero, and r is the distance between two atoms. The parameters σ and ε depend on the types of atoms being considered. For CNTs, the Lennard-Jones parameters are the same as for graphite ($\sigma = 3.4$ Å and $\varepsilon = 4$ meV). The Lennard-Jones parameters for PE are based on Reference 11 where the values for C and H atoms are listed. When the two atoms are the same, then Lennard-Jones parameter values can be used as listed; however, for atoms that are different (or in the case of C atoms that have different hybridizations), the interaction must be calculated using the Lorentz-Berthelot mixing rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$

and

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right)$$

where, i and j are the atom subscripts.

Simulations are performed using LAMMPS simulation software. Periodic boundary conditions are maintained in all directions. The time step used for minimization is 0.1 femtosecond. Each system's energy is first minimized using the conjugate gradient method. The appendix contains a sample of the minimization script.

V. RESULTS

As a comparison to Reference 12, a PE matrix is modeled to begin the proof of concept. Minimization is performed on the polymer matrix using the minimization command available in LAMMPS. Figure 5 shows the effectiveness of energy minimization to make a more compact structure. Green represents the C atoms, and gray represents the H atoms. Minimization, which finds the configuration with the lowest potential energy for the system, is a necessary step since a simulation that starts at a high energy will likely become unstable and the system will "blow up." PE in a volume of 40 nanometers squared by 100 nanometers in length is chosen. The minimized structure is shown in Figure 6, along with a plot of its energy minimization versus time step. The energy begins as a positive value since the forces are calculated between each pair of atoms using the interatomic potential. The minimization algorithm moves the atoms a small time step to incrementally adjust the position of the atoms to an equilibrium position, which is not too close to cause repulsion nor too far to cause attraction. The largest reductions in energy occur in the first few time steps. Similarly, the before and after minimization structures of the composite are shown in Figure 7. The composite's volume is 80 nanometers squared by 100 nanometers, which allows the inclusion of the SWNT. Since the CNT fills the center of the PE matrix, the compact minimization does not occur like with the PE alone. In the case of the composite, the minimization efforts are less obvious; however, the decreasing total energy in Figure 8 verifies that minimization did occur.
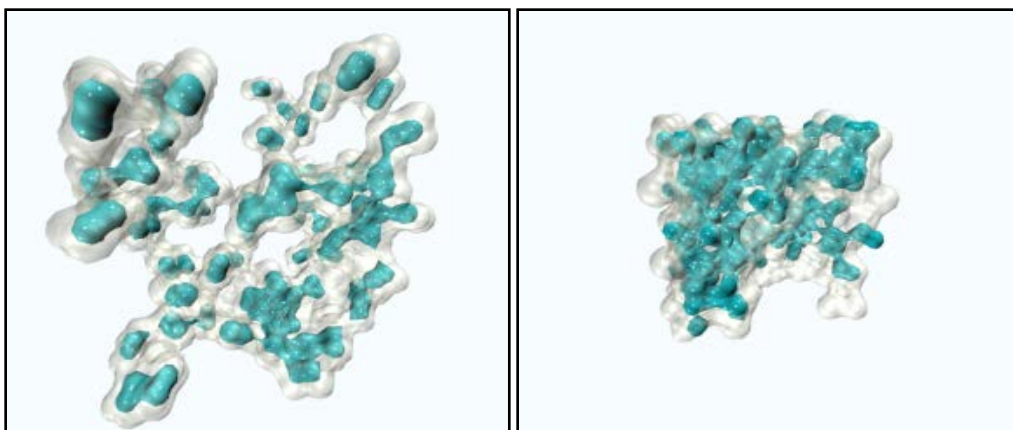
(a) Before Energy Minimization   *(b) After Energy Minimization*

*Figure 5. Minimization Results Shown for 80 Ethylene Molecules
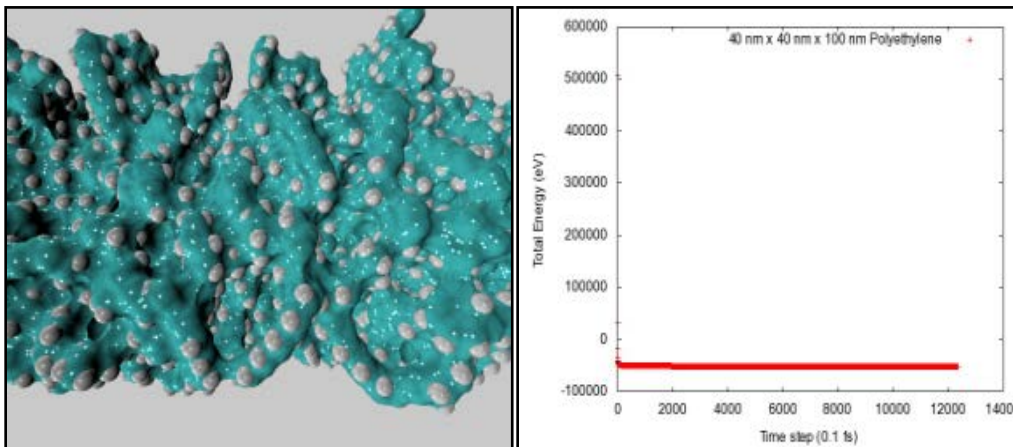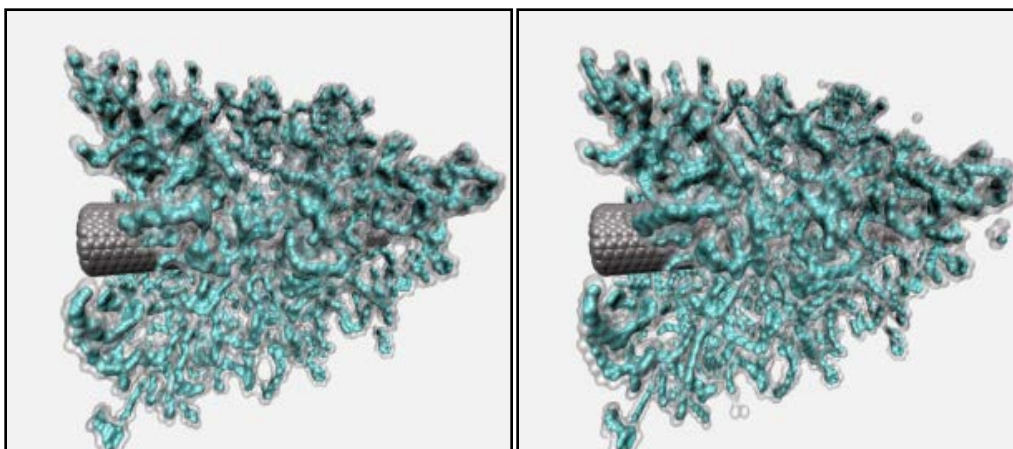(Green, C Atoms; Gray, H Atoms)*

*Figure 6. Compacted Block (40-by-40-by-100 Nanometers)
of PE After Total Energy Minimization*

(a) Before Minimization   *(b) After Minimization*
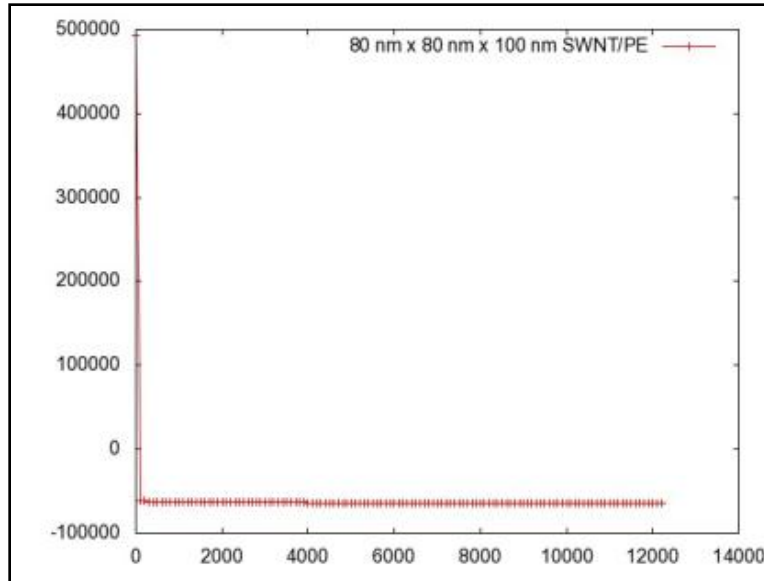
Figure 7. PE/SWNT Composite

Figure 8. Energy Minimization of Total Energy of PE/SWNT Composite

VI. CONCLUSIONS

Several strides were made in studying the PE and nanocomposite models. An initial configuration was able to be established for PE and a PE/SWNT composite. Since an appropriate interatomic potential was chosen (the AIREBO potential), minimization was performed on both systems. Minimization of the PE structure did result in a more compact lower energy configuration; however, both structures' total energy decreased significantly during the minimization process. The modeling of polymers is a computationally expensive process which requires more computing power than the office desktop system that was available for the project.

VII. FUTURE DIRECTIONS

Due to time constraints, additional tasks were not able to be completed but nonetheless are needed to understand thermal transport at the composite interface. Additional models that need to be considered include arrays of SWNTs since the actual thermal interface incorporates aligned CNTs. To extend this concept further, Multi-Walled Carbon Nanotubes (MWNTs) should be modeled as well and in an arrayed geometry. The typical CNT is multi-walled; therefore, double- or triple-walled CNTs should be useful in establishing trends. The actual thermal conductivity measurements were performed using the constant energy NEMD method mentioned in Section II.

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LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

AIREBO	Adaptive Intermolecular Reactive Empirical Bond Order
C	carbon
CNT	carbon nanotube
H	hydrogen
LAMMPS	Large-Scale Atomic and Molecular Massively Parallel Simulator
MD	Molecular Dynamics
MWNT	Multi-Walled Carbon Nanotube
NEMD	Non-Equalibrium Molecular Dynamics
PDB	Protein Data Bank
PE	polyethylene
REBO	Reactive Empirical Bond Order
SWNT	Single-Wall Nanotube
TLPS	Transient Liquid Phase Sintering
VMD	Visual Molecular Dynamics

APPENDIX
EXAMPLE SCRIPTS

A.1 Example TubeGen Script

```
set relax_tube yes
set format xyz
set units angstrom
set element1 C
set element2 C
set bond 1.4210
set shape hexagonal
set chirality 10,10
set gutter 10, 10, 0
set cell_count 1, 1, 41
generate
save cnt.xyz
exit
```

A.2 Example Packmol Script

```
tolerance 2.0
seed 1211984
output polyethylene_cylindrical_void.pdb
filetype pdb
nloop 1000

structure ethylene_10.pdb
        number 266
        inside box  0. 0. 0. 80. 80. 100.
        outside cylinder 40. 40. 0. 0. 0. 1. 15. 100.
end structure
```

A.3 Example LAMMPS minimization Script

```
clear
log log.polyethylene_minimize
###Minimization of PE####
units           metal
boundary        p p p
atom_style      atomic

pair_style airebo 3.0 1 1
read_data       crystal/polyethylene_box
pair_coeff * *   ../LAMMPS/lammps-17Jun11/potentials/CH.airebo C H

neighbor 2.0 bin
neigh_modify every 3 delay 3
```

timestep 0.0001

#####MINIMIZATION#####
dump 1 all custom 5000 /scratch/walkere1/dump.polyethylene id type x y z
dump 2 all xyz 5000 /scratch/walkere1/dump.polyethylene.xyz
thermo 2
thermo_style custom step temp ke etotal pe vol
minimize 0.0 1.0e-8 100000 100000

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